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INTERLABORATORY EVALUATION OF T_g OF AMBIENT-CURED EPOXIES USED IN CIVIL INFRASTRUCTURE

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ABSTRACT: Ambient-cured epoxies used to bond high strength continuous fibers to concrete for strengthening purposes can have glass transition temperatures (T_g) that are not only close to the service temperature but can also change over time as a function of environmental conditions. While the design ramifications of using such an epoxy resin with an evolving T_g close to the service temperature are unclear and difficult to predict, recommended methods for assigning a T_g for such resins are nonetheless needed. In the present investigation, an interlaboratory evaluation of T_g characteristics of several ambient-cured epoxy resins using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) was carried out. The need for standardized specimen conditioning prior to T_g measurement is demonstrated. Of the three DMA T_g methods employed, the $\tan \delta$ method provided the lowest standard deviation. Because of its reliability and its roots in mechanical testing, the DMA $\tan \delta$ method applied during a single temperature up-ramp is recommended for assigning T_g .

1. Introduction

Fiber reinforced polymer (FRP) composites are increasingly used to strengthen, repair, and retrofit (hereafter, simply “strengthen”) deficient concrete structures in civil infrastructure. One of the key economic attractions of the technique is the ease with which strips of dry fibers can be impregnated with a two-part thermosetting polymer resin and bonded to the surface of the structure with minimal labor costs, construction infrastructure, and disruption of use of the structure. Two broad categories of FRP strengthening are “contact-critical” applications (e.g., providing confinement to concrete columns) and “bond-critical” applications (e.g., supplementary flexural or shear reinforcement in concrete beams, walls, slabs, and beam/column connections). “Bond-critical” implies that resistance against debonding or slip is essential for successful external strengthening. Both categories depend on the excellent tensile-stress-carrying capability of the fibers. However, in the bond-critical category, the integrity of the polymer resins saturating the fibers and bonding the fibers to the structure is also of great importance in the performance of the system. To-date, numerous documents on the design of externally bonded FRP reinforcement systems for concrete and masonry structures have been published worldwide (e.g., see the “Design Codes and Guidelines” list at the IIFC website, <http://www.iifc-hq.org/publications/code-references/>).

In the United States, Committee 440 (Fiber Reinforced Polymer Reinforcement) of the American Concrete Institute, and subcommittee 440-F (FRP Repair/Strengthening) in particular, have played a prominent role in the development of guides for designing externally bonded FRP reinforcement for concrete structures. An area of needed research identified by 440-F is methods of characterizing and comparing epoxy

primers, saturants, and adhesives for their potential use in warm environments. “Warm” in this context means temperatures of up to $\sim 45^{\circ}\text{C}$ (i.e., not “fire”) that may be encountered in certain industrial buildings and outdoor structures, for example. Current guidance in ACI 440.2R-08 (2008) recommends that the maximum service temperature of FRP strengthening systems be limited to $T_g - 15^{\circ}\text{C}$, where T_g is the lowest glass transition temperature of the various resins that may be used in a given system. This recommendation stems from recognition of the reduced adhesive and cohesive strength of polymers as they soften near their primary glassy-rubbery transition regime (T_g), which is usually in the range of $40\text{--}80^{\circ}\text{C}$ for ambient curing epoxy resins developed for field application. It is further recommended that T_g be obtained from the manufacturer of the resin or by testing using any of five different references mentioned in ACI 440.2R-08. These references include standard test methods for T_g by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC), a standard practice citing over a dozen different approaches for obtaining T_g by DMA (ASTM D4065, 2012), and two tangentially related test methods for heat distortion temperature (HDT). The test methods and their associated references are listed in Table 1. As can be confirmed by reading these documents, the test results depend on the details of the somewhat flexible material preparation and test procedures. Important details for material preparation include the degree of cure and moisture content. Important details in DMA testing include the loading mode (e.g., tension vs. flexure), loading frequency, temperature rate, and the type of data used to assign T_g (e.g., onset storage modulus, midpoint storage modulus, loss modulus peak, $\tan \delta$ peak). Important details in DSC testing include the specimen size, specimen machining method, and temperature rate.

In an attempt to avoid the confusion that can result from using different test methods to compare different materials tested in different laboratories, a task group was formed within ACI 440-F to: (1) examine common test methods adopted by the community and determine which would be most readily accepted for comparing the warm-temperature capabilities of typical ambient-cured epoxies used in FRP strengthening; (2) recommend a single set of critical test details to ensure valid material comparisons; and (3) re-visit the “ T_g -x” question in light of the previous steps to determine if x should be a temperature other than 15°C . The present paper briefly mentions the outcome of the first objective and mainly reports progress on the second objective. The task group has not considered the third objective, to-date.

2. Approach

The initial work of the task group focussed on narrowing down the scope of test methods that would subsequently receive detailed consideration. In addition to the DMA, DSC, and HDT methods mentioned previously, the group considered thermomechanical analysis (TMA) (see Table 1). Since most of the data available to the group was from DMA and DSC testing, these two methods for T_g were selected for further consideration. Based on an informal assessment, these test methods seem to be acceptable to researchers, practitioners, and material suppliers involved in the field of FRP strengthening.

DMA and DSC T_g test results for 14 different ambient-cure epoxy systems used for FRP strengthening, obtained in three different academic laboratories, were analyzed. To avoid the mention of commercial names, the materials are denoted by letters A through M in Table 2. Materials labelled with a “prime” symbol are nominally the same as the “unprimed” material, but are distinguished because they were obtained from different suppliers in different parts of the world and were tested in different laboratories. The laboratories that performed the testing are denoted by numerals 1 through 3. For DMA testing, commercial saturants and adhesives were roughly equally represented, although two commercial primers were tested as well. For DSC testing, the data are split between commercial saturants and a generic epoxy system that cures at room temperature. In total, 64 sets of data were obtained using DMA and 55 using DSC.

DMA testing was used to assign T_g based on the onset of reduction of storage modulus, $(T_g)_{\text{SM}}$, peak loss modulus, $(T_g)_{\text{LM}}$, and peak $\tan \delta$, $(T_g)_{\text{TD}}$ as measured in the first temperature up-ramp. Note that T_g based on the onset of reduction of loss modulus is more conservative than T_g based on the loss modulus transition midpoint. Loading was either by tension at 5 Hz or single-clamped cantilever flexure at 1 Hz. Temperature was ramped at $3^{\circ}\text{C}/\text{min}$. in the tension tests and $2^{\circ}\text{C}/\text{min}$. in the flexure tests. Insufficient data were available to evaluate the separate effects of loading mode, frequency, and temperature ramp rate.

Table 1 – Original test methods considered.

Test	Reference	Principal
DMA T_g	ASTM E1640 (2009)	Dynamic stress-strain behavior vs. temperature
DSC T_g	ASTM E1356 (2008)	Specific heat capacity vs. temperature
HDT	ASTM D648 (2007); ASTM D2092 (2013)	Temperature at which a certain deflection is met under a certain load
TMA T_g	ASTM E1824 (2013); ASTM E1545 (2011)	Thermal expansion coefficient vs. temperature

Table 2 – T_g database.

Material	Laboratory	Test Type
A	1	DMA, DSC
B	1	DMA, DSC
B'	2	DMA
C	2, 3	DMA (Lab. 2), DSC (Lab. 3)
D	3	DSC
E	2	DMA
F	2	DMA
G	2	DMA
H	2	DMA
I	2	DMA
J'	2	DMA
K	2	DMA
L	1	DMA
M	1	DMA

DSC testing was used to assign T_g based on the midpoint of the transition range measured in the first temperature up-ramp. The temperature ramp rate in all cases was 10°C/min. Sample size was always between 5 and 10 g. One laboratory prepared samples by cutting 2-mm pieces from larger stock, while the other cast the resin directly into the sample pans. The pans were sealed in all cases. Since there was no overlap in the materials tested in the two laboratories providing DSC data, the effects of sample preparation method could not be determined.

3. Observations

Twenty-nine DMA scans of different materials, curing temperatures, and curing times were analyzed to determine typical differences between T_g values assigned based on storage modulus, loss modulus, and $\tan \delta$. In general, it was found that $(T_g)_{SM} < (T_g)_{LM} < (T_g)_{TD}$. Table 3 lists the average difference among the various measures of T_g as well as the standard deviation of the differences.

Table 3 – Comparison of methods of T_g assignment by DMA testing.

Difference in T_g by Method	Average (°C)	Standard Deviation (°C)
$(T_g)_{LM} - (T_g)_{SM}$	10.5	5.6
$(T_g)_{TD} - (T_g)_{LM}$	12.6	5.1
$(T_g)_{TD} - (T_g)_{SM}$	23.1	9.1

Three different batches of Resin B were mixed and tested after 7, 30, and 100 days of curing at room temperature to assess the repeatability of T_g values by different DMA methods (Table 4). Based on the standard deviation across batches at a given curing time, it is seen that $\tan \delta$ is the most consistent method (std. dev. 1-5°C). The average data from Table 4 are presented in a bar chart format in Fig. 1, where the notable increase in T_g with curing time can be visualized.

Three batches of Resin B—each cured for 7, 30, and 100 days at room temperature—were also evaluated by DSC (Fig. 2). As with DMA, the increase in DSC T_g with curing time is apparent. The standard deviation was exceptionally low (1-2°C for two sets of 3 repetitions each). A general conclusion on the rank of DSC T_g in relation to the three DMA T_g values across all curing times could not be discerned with the available data.

Table 4 – Effects of batch variability, DMA method, and curing time on T_g . Resin B cured at room temperature.

Curing Time (Days)	Batch	$(T_g)_{SM} (^{\circ}\text{C})$	$(T_g)_{LM} (^{\circ}\text{C})$	$(T_g)_{TD} (^{\circ}\text{C})$
7	A	42	47	59
	B	43	49	60
	C	36	44	57
	Average	40	47	59
	Std. Dev.	3.8	2.5	1.5
30	A	51	56	65
	B	48	51	63
	C	48	53	64
	Average	49	53	64
	Std. Dev.	1.7	2.5	1.0
100	A	59	64	73
	B	52	56	66
	Average	56	60	70
	Std. Dev.	4.9	5.7	4.9

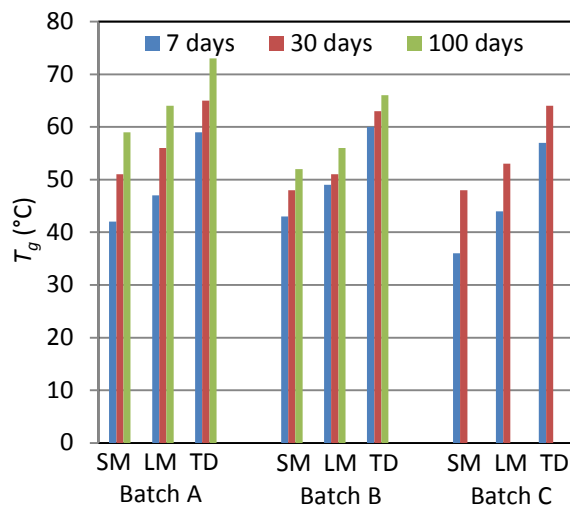


Fig. 1 – DMA T_g of Multiple Batches of Resin B Cured at Room Temperature for Various Times

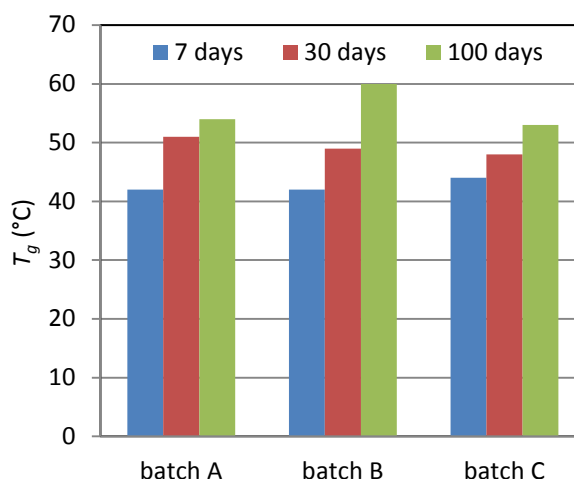


Fig. 2 – DSC T_g of Multiple Batches of Resin B Cured at Room Temperature for Various Times

Subjecting epoxy resins to an elevated temperature after some period of curing at a lower temperature can accomplish post-curing, in which case T_g should increase over the non-post-cured material. Figure 3 shows DMA T_g values for Resin B' that was cured for slightly more than 30 days at room temperature and then subjected to a 6-hour post cure in air at 80°C. It is seen that even a short exposure to an elevated temperature after a month of cure at room temperature is sufficient to increase the T_g of this particular resin by 5-10°C. It is therefore clear that the temperature ramps used to measure T_g (which by definition must exceed the T_g) may alter the T_g . This is why T_g can only be sensibly measured on the first temperature up-ramp.

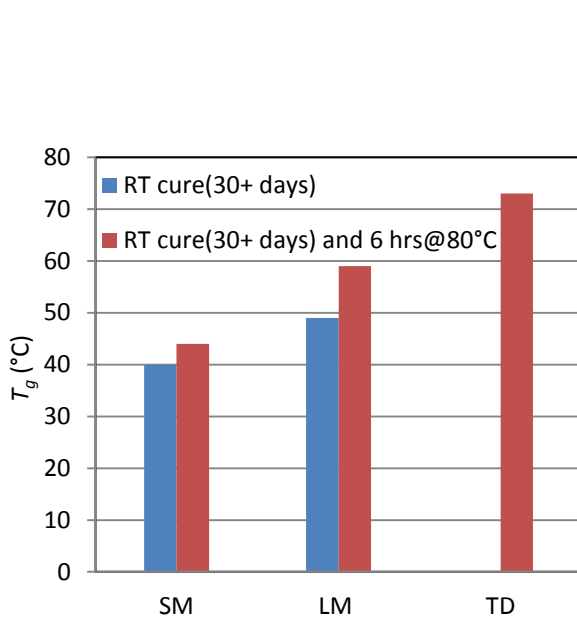


Fig. 3 – DMA T_g of Resin B' with and without a 6 hour 80°C Exposure Following 30 Days of Cure at Room Temperature (RT)

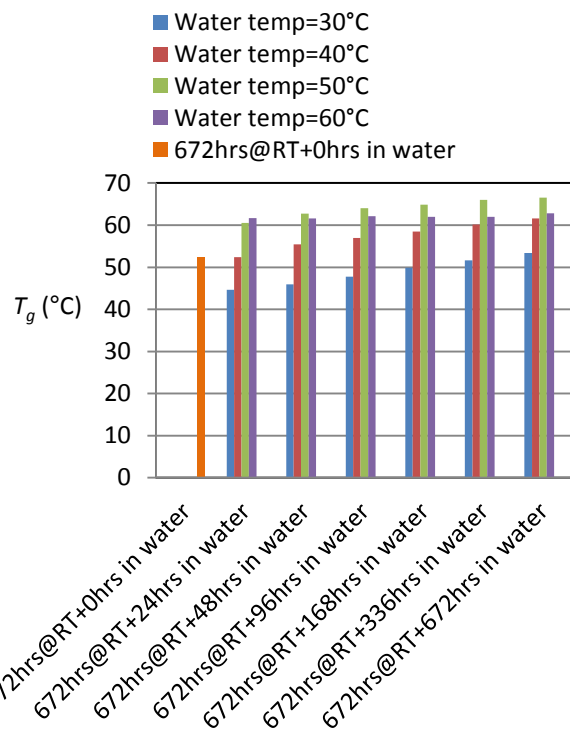


Fig. 4 – DSC T_g of Resin C Cured for 672 hours in Room Temperature Air Plus Various Times in Water at Various Temperatures

Figure 4 shows the influence of exposure to water on DSC T_g following 672 hours of cure at room temperature, in air. For the water exposure, duration ranged from 0 hours to 672 hours and temperature ranged from 30°C to 60°C. Equilibrium values of T_g are reached at shorter durations of water exposure as the water temperature increases. The immediate effect of exposure to water at 30°C is to reduce T_g . The original T_g prior to 30°C water exposure is not recovered until approximately the 672 hour time period. Exposure to intermediate temperatures of 40°C and 50°C increased T_g in direct proportion to the exposure temperature and period of time. After 96 hours, the 50°C water exposure led to higher T_g values versus those seen at any other water temperature, including 60°C, for any duration investigated. These results suggest that 60°C water may prevent attainment of maximal T_g in this epoxy material. Possible explanations for such behavior could be cure inhibition or material degradation.

4. Recommendations

Recommendations were drawn based on the literature and by evaluating T_g values for a variety of ambient-cured epoxy resins according to DMA and DSC test methods.

- The age, environmental history, and geometry of ambient-cured epoxy T_g specimens should be standardized, as should the test method employed, including details such as loading rate, loading mode, and temperature ramp rate. These recommendations are based on common knowledge in polymer characterization.
- Due to the need to exceed the T_g in order to measure T_g , along with the possibility that ambient-cured epoxies may post-cure at temperatures above the T_g , only the first temperature up-ramp is useful for measuring the T_g of ambient-cured epoxies.

- Because of the low scatter in T_g obtained by the $\tan \delta$ method of DMA and the mechanical nature of the test, the $\tan \delta$ method is recommended for use with ambient-cured epoxies. The low scatter of DSC T_g measurements makes DSC a potential alternate choice. The T_g method selected for use should be particular to the value of “x” in the “ T_g -x” service temperature limit for the resin system.
- The fact that ambient-cured epoxies continue to gain in T_g for several weeks, if not years, will need to be reconciled with T_g recommendations in design guidelines. At this time, it is not clear that an “inadequate” T_g over a limited time is or is not a detriment to the expected serviceability of an FRP strengthening system.
- Exposure of an epoxy resin cured for one month at room temperature to warmer air or water for even a short time can increase T_g substantially. Excessive temperature in conjunction with water immersion can reduce this increase. Relationships between T_g values reached during real service conditions and so-called “accelerated” conditions need to be investigated.

A few of these recommendations are neither unique to ambient-cured epoxies nor novel in polymer science. Nonetheless, the full set of recommendations provides a useful base of experience for structural engineers aiming to understand T_g testing and test results in the context of ambient-cured epoxies.

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